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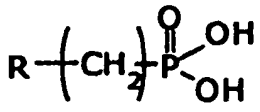
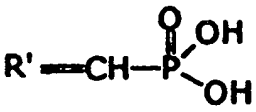
(54) Title: PHOSPHONIC ACID REACTION PRODUCTS AND USE IN COATING COMPOSITIONS

(57) Abstract

The invention provides an aqueous coating composition comprising nonionically and/or anionically stabilized film–forming polymers and metallic pigments and a compound which is the reaction product of a phosphonic acid derivative, a hydroxy–functional addition polymers and, optionally a compound having a hydroxy group, in which the phosphonic acid derivative is selected from one or both of (I) and (II), wherein R and R' are selected from the group consisting of an aliphatic and an aromatic substituent having 1 to 25 carbon atoms optionally including heteroatoms of at least one of oxygen, phosphorus and silicon.



(I)



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TITLE

PHOSPHONIC ACID REACTION PRODUCTS AND USE IN COATING COMPOSITONS

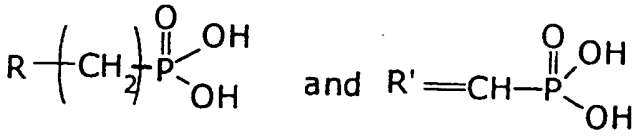
BACKGROUND OF THE INVENTION

U.S. 4,675,358 discloses coating compositions employing phosphoric acid derivatives. Such compositions are not very hydrolytically stable. WO 96/08518 describ derivatives and their use in waterb d compatibility with other binders g linkages. EP 391,230 disclose of an alpha-aminomethylene phosph l containing at least one epoxy group. in water-borne compositions that are destabilizes the coating compos llic coating compositions comprising acrylic copolymers to reduce the gassing of aluminum flakes. Such compositions have limited hydrolytic stability and limited effectiveness.

SUMMARY OF THE INVENTION

We have found that hydrophobic-substituted phosphonic acid derivatives which are reaction products with hydroxy-functional copolymers are particularly effective for inhibiting the corrosion of metallic pigments in water-borne compositions. The invention concerns an aqueous coating composition comprising a stabilized film-forming polymer, a metallic pigment and a compound which is the reaction production of a, b and optionally c, wherein:

(a) is 5 to 95 weight percent of a phosphonic acid derivative consisting of one or both of



wherein R and R' are selected from the group consisting of an aliphatic, cycloaliphatic and aromatic substituent having 1 to 25 carbon atoms and optionally up to 10 heteroatoms of at least one of oxygen, phosphorus and silicon;

(b) is 5 to 95 weight percent of a hydroxy-functional addition polymer with a weight average molecular weight of 1000 to 30,000; and

(c) is 0 to 90 weight percent of a compound having one hydroxy-functional group.

Representative examples of phosphonic acid group-containing compounds are vinyl phosphonic acid, propyl and octyl phosphonic acid, and hydroxyethane diphosphonic acid.

Representative examples of hydroxy-functional polymers are addition copolymers of methacrylates, vinylaromatics, acrylates, acrylamides/methacrylamides and their derivatives, acrylonitrile, methacrylonitrile, allylalcohol, maleates, itaconates and vinyl monomers. The copolymers are hydroxy and/or acid functional . Typical comonomers useful to obtain the hydroxy-functionality are 2-hydroxy ethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxy propyl acrylate, 2-hydroxy propyl methacrylate, allyl alcohol, 1,4 butenediol, 4-hydroxybutyl acrylate, bis-hydroxy ethyl maleate and the like. Preferred hydroxy-functional copolymers are copolymers of styrene and allyl alcohol. A preferred phosponic acid derivative is propyl and octyl phosphonic acid.

The hydroxy functional copolymers are typically prepared in a free-radical initiated process using peroxy or azo initiators. The reaction between the hydroxy functional copolymer and the vinyl and/or alkyl phosphonic acid can be run in a fusion or solvent process where water is distilled.

The reaction products of the phosphonic acid derivatives and the hydroxy-functional copolymers are used to treat metallic pigments before the final blend is inverted in water. The final metallic pigment dispersions are stable from gassing.

DETAILED DESCRIPTION

Preferred coating compositions are the following:

where the reaction product as corrosion inhibitor is used in the form of a salt;

where the phosphonic acid derivative is propyl, octyl or vinylphosphonic acid;

where the hydroxy-functional product is based on a styrene-allyl copolymer;

where the corrosion inhibitor based on phosphonic acid has an acid value of 25 to 400 mgKOH/g;

where the composition is anionically or non-ionically stabilized, and

where the film-forming polymers are anionically stabilized vinyl, acrylic and/or urethane emulsions.

Preferred phosphonic acid group-containing reaction products are those formed from one or more of vinyl phosphonic acid, propyl and octyl

phosphonic acid, and hydroxyethane diphosphonic acid with one or more hydroxy-functional copolymers of styrene and allyl alcohol. Preferably, R and R' have up to 12 carbon atoms and effect good hydrophobic-lipophilic balance (HLB).

EXAMPLES

Example 1

In a reaction vessel fitted with stirrer, thermometer, reflux condenser and Dean and Stark separator, a mixture of 300 parts xylene, 300 parts styrene/allyl alcohol copolymer with a molecular weight of 1600 was heated at 85-90°C till dissolved. There was then added 129.33 parts of octyl phosphonic acid (80% solution in water/ethanol=1/1). The temperature was raised to reflux (± 148°C) while water was removed. After 2 hours, 16 parts of water had been removed and the contents of the reactor were vacuum stripped. The reaction product was diluted with 270 parts of 2-butoxyethanol.

Test results:

Solids	58.8%
Viscosity (Gardner Holdt)	W
Acid value	148 mgKOH/g
Number Average MW	1700
Weight Average MW	4400

Example 2

Procedure of Example 1 was repeated using 300 parts xylene, 300 parts styrene/allyl alcohol, 215.55 parts octyl phosphonic acid. In total, 28 parts of water were stripped in about 2 hours. After vacuum stripping, the reaction product was diluted in 310 parts of 2-butoxyethanol.

Test results:

Solids	59.7%
Viscosity (Gardner Holdt)	V - 1/4
Acid value	188 mgKOH/g
Number Average MW	1300
Weight Average MW	3800

Example 3

Procedure of Example 1 was repeated in which 240 parts styrene/allyl alcohol copolymer were reacted with 73.8 parts of p-tert amylphenol and 137.33 parts of Cublen® K60 in 350 parts of xylene. Cublen® K60 is a 60% solution in

water of hydroxy ethane diphosphonic acid from Zschimmer and Schwarz Company.

Test results:

Solids	58.4%
Viscosity	Y
Acid value	184 mgKOH/g
Number Average MW	1560
Weight Average MW	4260

Example 4

Procedure of Example 1 was repeated in which 100 parts xylene, 300 parts of styrene/allyl alcohol copolymer and 85 parts of vinylphosphonic acid were used.

Test results:

Solids	59.8%
Viscosity	Z2
Acid value	178 mgKOH/g
Number Average MW	1100
Weight Average MW	2400

Example 5

Styrene/Allylic Alcohol Copolymer Modified with Propyl Phosphonic Acid

Into a 500 ml 3-neck round bottom flask fitted with a reflux condenser, water separator and air-driven stirrer, place the following and heat to 85°-90°C until dissolved:

Xylene	50.0 grams
ARCO SAA100 resin	100.0 grams

Add the following and raise temperature to reflux (~148°C):

propyl phosphonic acid	36.2 grams

Continue to heat for 2 to 3 hours when approximately 5.6 grams of water will have been removed by azeotropic distillation. Cool to 100°C and begin vacuum strip to remove about 50 grams of solvent. At the end of the distillation, add the following to the reactor and allow to cool.

Butylcellosolve	90.0 grams

Fill out into a plastic container.

Product

Acid Number	145
Weight Solids	59%

Example 6

Paint Example:	Parts:
Dispersions	
Passivator Example 2	7.83
Butyl Glycol	58.42
Alu Flake (1)	30.75
Dimethylethanolamine	1.50
Thickener (2)	1.50
Aluminum Based Paint	
Dispersion of Passivator of Example 2	24.03
Latex (3)	27.53
D.I. water	47.55
Defoamer (4)	0.01
Thickener Combination (5)	0.88
Gassing Results (6)	
After 1 week	OK
After 2 weeks	OK
After 3 weeks	OK
After 4 weeks	OK

(1) Stapa Metallic R-607/Eckart

(2) NOPCO DSX 1550/Henkel

(3) Latex Anionically Stabilized/DuPont

(4) Balab 3056A/Witco

(5) ASE-60/Polyphobe PP-107 :78/22. Rohm & Haas/Union Carbide

(6) ALU Paint is mixed with iron oxide dispersion and kept in closed container at 49°C.

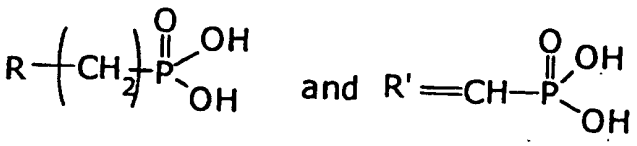
Example 7

Paint Formula:	Parts:
Mineral spirits (boiling range 140-160°C)	4.9
Ethylene glycol-mono-n-hexylether	4.9
Ethylene glycol-mono-n-butylether	10.9
Aluminum Flake (Silverline® SSP-353) (course aluminum flake 70% solids)	17.8
Inhibitor of Example 2	4.3
Acrylic latex 30% in water	61.5
(Adjust till pH is 9) with aminomethylpropanol	0.90
The gassing was followed by measuring the ml of hydrogen (H_2) generated in 16 hours at 60°C.	5.3 ml

WHAT IS CLAIMED IS:

1. An aqueous coating composition comprising a stabilized film-forming polymer, a metallic pigment and a compound which is the reaction product of (a), (b) and optionally (c), wherein:

(a) is 5 to 95 weight percent of a phosphonic acid derivative consisting of one or both of



wherein R and R' are selected from the group consisting of an aliphatic, cycloaliphatic and aromatic substituent having 1 to 25 carbon atoms and optionally up to 10 heteroatoms of at least one of oxygen, phosphorus and silicon;

(b) is 5 to 95 weight percent of a hydroxy-functional addition polymer with a weight average molecular weight of 1000 to 30,000; and

(c) is 0 to 90 weight percent of a compound having one hydroxy-functional group.

2. A composition of Claim 1 where the reaction product is in the form of a salt.

3. A composition of Claim 1 where the phosphonic acid derivative is propyl, octyl or vinylphosphonic acid.

4. A composition of Claim 1 where the hydroxy-functional product is based on a styrene-allyl alcohol copolymer.

5. A composition of Claim 1 where the corrosion inhibitor based on phosphonic acid has an acid value of 25 to 400 mgKOH/g.

6. A composition of Claim 1 where the film-forming polymers are selected from anionically stabilized vinyl, acrylic and urethane emulsions.

7. A composition of Claim 1 where the phosphonic acid group-containing reaction products are formed from one or more members selected from the groups consisting of vinyl phosphonic acid, propyl phosphonic acid, octyl phosphonic acid and hydroxyethane diphosphonic acid with one or more members selected from the group consisting of hydroxy-functional copolymers of styrene and allyl alcohol.

8. A composition of Claim 7 comprising copolymers of styrene/allyl alcohol and propyl phosphonic acid.

9. A composition of Claim 1 which is anionically stabilized.

10. A composition of Claim 1 which is nonionically stabilized.

INTERNATIONAL SEARCH RE. RT

Int tional Application No
PCT/US 98/15761

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F8/40 C09D5/38 C09C1/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D C08F C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 5 637 441 A (BRENK MICHAEL ET AL) 10 June 1997 see column 3, line 49 - column 4, line 11	1
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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